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<p>(21) International Application Number: PCT/GB93/02280 (22) International Filing Date: 4 November 1993 (04.11.93) (30) Priority data: 9223351.9 6 November 1992 (06.11.92) GB (71) Applicant (for all designated States except US): ZENECA LIMITED [GB/GB]; Imperial Chemical House, 9 Millbank, London SW1P 3JF (GB). (72) Inventor; and (75) Inventor/Applicant (for US only) : HAMMOND, Timothy [GB/GB]; 12 Cragside, Sedgfield, Stockton on Tees, Cleveland TS21 2DQ (GB). (74) Agents: MANNION, Sally, Kim et al.; Group Patent Services Department, P.O. Box 6, Shire Park, Welwyn Garden City, Hertfordshire AL7 1HD (GB).</p>		<p>(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, LV, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  Published Without international search report and to be republished upon receipt of that report.</p>
<p>(54) Title: POLYMER COMPOSITION CONTAINING POLYHYDROXYALKANOATE AND METAL COMPOUND</p> <p>(57) Abstract</p> <p>Polymer compositions are provided which comprise a first polyhydroxyalkanoate component and optionally a second polymer component, the composition have enhanced properties by using an inorganic oxygen containing compound in the composition. The inorganic oxygen containing compound may be acting as a transesterification catalyst.</p> <p style="text-align: center;">26 9,6-32 34-69</p>		

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**POLYESTERS**

This invention relates to polyesters and in particular to compositions comprising polyesters and inorganic oxygen containing compounds.

It is a common problem with certain blends of more than one polyester that the polyesters are not compatible and the resultant blend has inferior properties to the separate blends. Transesterification is a method by which an ester is transformed into another through interchange of the alkoxy moiety. It is not only applicable to pure organic synthesis but also to polymerisation techniques. For example the reaction between dimethyl terephthalate and ethylene glycol was important in polyester production in the middle of this century. Metal alkoxide catalysts are known to transesterify certain materials (Chemical Reviews, 1993. Vol 93 No. 4 pages 1449-1470) and in the case of poly-(R)-3-hydroxybutanoic acid, degradation to the monomeric building blocks was achieved.

It has now been found that transesterification catalysts can be used in blends of different polyesters to increase compatibility and hence improve physical properties of such blends. Such compounds may also be used to maintain or increase the molecular weight of a blend of the same or different polymers or to increase the resulting melt viscosity of blends of polymers whose individual components have widely differing melt viscosities.

Thus, according to the present invention there is provided a polymer composition comprising a first polyester component which is at least one polyhydroxyalkanoate (PHA) and a second polymer component, and at least one oxygen containing compound of a metal or metalloid selected from Groups IA, IIA, IIIA, IVA, VA, VIA, VIIA, VIII, IB, IIIB, VB and VIB of the Periodic Table.

The oxygen containing compound (hereinafter referred to as "oxy compound") is preferably a transesterification catalyst or a precursor thereof. (The Periodic Table referred to is as in "Abridgements of Patent Specifications" published by the British Patent Office).

In a second aspect of the invention there is provided a polymer composition comprising a first polyester component which is at least one PHA and at least one second polymer component, and at least one oxy compound of a metal or metalloid selected from Group IIB of the Periodic Table; provided that when the first polyester component is poly(hydroxybutyrate) the second polymer component is not polycaprolactone.

The first polyester component is preferably capable of a relatively high level of crystallinity, for example over 30%, especially 50-90%, in the absence

of plasticiser. Suitably such polyesters include polyhydroxyalkanoates (PHA), a polyglycollic acid or polylactic acid or a synthetic polypropiolactone, polybutyrolactone, polyvalerolactone, polycaprolactone or a caprolactone copolymer.

5           Suitable PHAs will be or include at least one having units of formula I:



where  $m$  is in the range 1-13 and  $n$  is  $2m$  or (if  $m$  is at least 2)  $2m-2$ . Typically  $C_m H_n$  contains 2-5 carbon atoms in the polymer chain and the remainder (if any) in a side chain. In very suitable polyesters  $n$  is  $2m$  and especially there are units with  $m = 3$  and  $m = 4$  copolymerised and with respectively a  $C_1$  and  $C_2$  side chain on the carbon next to oxygen in the chain. Particular polyesters contain a preponderance of  $m = 3$  units, especially with 70-95 mol% of such units, the balance being units in which  $m = 4$ . The molecular weight  $M_w$  of the PHA is for example over 50000, especially over 100000, up to eg  $2 \times 10^6$ .

15           In PHAs having units with  $m = 3$  and  $m = 4$  there may be very small, typically fractional, percentages of units having higher values of  $m$ . PHA consisting essentially of  $m = 3$  units is poly-3-(R)-hydroxybutyrate (PHB), and PHA consisting of  $m = 3$  and 4 units is polyhydroxybutyrate-co-valerate (PHBV).

20           The PHA can be a product of fermentation, especially of a microbiological process in which a microorganism lays down PHA during normal growth or is caused to do so by cultivation in starvation of one or more nutrients necessary for cell multiplication. The microorganism may be wild or mutated or may have the necessary genetic material introduced into it. Alternatively the necessary genetic material may be harboured by an eukariote, to effect the microbiological process.

25           Examples of suitable microbiological processes are the following:

for Formula I material with  $m = 3$  or  $m =$  partly 3, partly 4 :

EP-A-69497 (Alcaligenes eutrophus)

for Formula I materials with  $m = 3$ :

30           US 4101533 (A. eutrophus H-16)

EP-A-144017 (A. latus);

for Formula I material with  $m = 7-13$ :

EP-A-0392687 (various Pseudomonas).

35           The PHA can be extracted from the fermentation product cells by means of an organic solvent, or the cellular protein material may be decomposed leaving microscopic granules of PHA. For specialised end uses the cellular protein may be partly or wholly allowed to remain with the PHA, but preferably

subjected to cell breakage.

Alternately the PHA may be synthesised by chemical processes known in the art. PHB can be prepared according to Bloembergen, S. and Holden, D. A., Macromolecules. 1989, Vol 22, p1656-1663. PHBV can be prepared according to Bloembergen, Holden, Bluhm, Hamer and Marchessault, Macromolecules. 1989, Vol 22, p1663-1669.

The second polymer component may be for example one or more of

- (a) a different production batch of same PHA;
- (b) a PHA of different composition;
- (c) a PHA as in (a) or (b) but with a different history, for example a different manufacturer or a different source, for example re-work or recycled or naturally occurring material;
- (d) when the first polyester component is microbiologically produced a synthetic polyester, for example a head-to-tail polyester or a substantially stoichiometric head-to-head tail-to-tail polyester. Likewise, when the first polyester component is synthetic the second polyester component can be microbiologically produced or a different synthetic polyester;
- (e) a synthetic polyester having only alcohol or phenol reactivity or only acyl reactivity;
- (f) other polymers, such as polyamides, having potential acylatable and or esterifiable groups.

If the second polyester component is type (b) it may have a crystalline melting point higher by at least 10°C, preferably at least 30°C, especially at least 50°C than that of the first polyester component. Very suitably the second polyester component consists of units according to Formula I of which at least 99 mol% have  $m = 3$  and the methyl side chain, that is, are substantially poly-3-R-hydroxybutyrate homopolymer. The first polyester component is then preferably the PHA containing 70-95, especially 82-95 mol%  $m = 3$  units, balance  $m = 4$  units. The first component polyester may itself be a blend of PHAs containing mol percentages of  $m = 3$  units in the range 50-98%, balance in each case  $m = 4$  units.

If the second polyester component is of type (d) it may be for example a poly-2-hydroxyalkanoate such as a polyglycolic acid or polylactic acid, or it may be a synthetic polypropiolactone, polybutyrolactone, polyvalerolactone, polycaprolactone or a caprolactone copolymer.

Examples of suitable synthetic polyesters are especially

polycaprolactone, polylactides, and polyesters containing combinations of dicarboxylic acids or derivatives thereof and diols. Dicarboxylic acids being selected from the group consisting of malonic, succinic, glutaric, adipic, pimelic, azelaic, sebacic, fumaric, 2,2-dimethylglutaric, suberic, 1,3-cyclopentane dicarboxylic, 1,4-dicyclohexane-dicarboxylic, 1,3-cyclohexane dicarboxylic, diglycolic, itaconic, maleic, 2,5-norbornane dicarboxylic and ester forming derivatives thereof and combinations thereof with diols selected from the group consisting of ethylene glycol, diethylene glycol, propylene glycol, 1,3-propanediol, 2,2-dimethyl-1,3-propanediol, 1,3 butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2,2,-trimethyl-1,6-hexanediol, thiodiethanol, 1,3-cyclohexanedimethanol, 1,4-cyclohexanedimethanol, 2,2,4,4- tetramethyl-1,3-cyclobutanediol, triethyleneglycol, tetraethyleneglycol, di-, tri-, tetra-propyleneglycol and combinations thereof. Also suitable are cellulose and cellulose acetates or butyrates, polypeptides, proteins and polyamides, and the copolymer of succinic acid and butylene glycol. The first polyester and second polymer components can be present in the composition in any suitable amount to provide the desired composition. Typically each component will be present in amounts from 5 - 90% w/w preferably 20% - 80% w/w.

The inorganic oxy compound may be for example a compound of an alkali metal, (for example sodium or potassium), an alkaline earth metal, (for example calcium), aluminium, silicon, phosphorus, titanium, germanium, arsenic, zirconium, tin or antimony. Titanium preferably has a valency of 4.

Preferably the inorganic oxy compound is an alkoxide, phenoxide, enolate or carboxylate particularly for example, titanium butoxide (n-, iso, or tert-) or titanium propoxide (n- or iso); the organic part of the compound is preferably chosen preferably to afford substantial involatility during melt processing of the PHA. If desired, the organic part may be partly polyvalent, for example derived from a polyhydric alcohol such as a glycol or glycerol or polyvinyl alcohol or a hydroxycarboxylic acid. Chelate compounds may be used. When carbon atoms are present typically the number of carbon atoms per inorganic atom is in the range 4 to 24. If desired, the compound can be introduced as oxide. A preferred oxide compound is antimony trioxide.

The above preferences in respect of the oxy compound apply to both aspects of the invention. For the second aspect composition the compound may preferably be of zinc or cadmium, especially a carboxylate, for example an acetate.

The content of the oxy compound in the composition is preferably in the



range 0.1 to 5 phr, at which levels it is effective as a transesterification catalyst.

5 In a preferred form of either aspect of the invention the composition comprises one or more reaction products of one or more of the first polyester component, second polyester component, other polyester component (if present) and the oxy compound. Such reaction product may be a decomposition product of the compound, and such reaction product may promote nucleation and thus crystallisation of the polyester.

10 Alternatively, the resulting reacted blend may give a more readily crystallisable polymer compared to that of an unreacted blend.

A further or additional alternative is that such a product may be the result of transesterification catalysed by the oxy compound or a decomposition product thereof. The transesterification product may be the result of redistributing the chain lengths and/or repeating unit combinations in a nominally single polyester. It may be the result of such redistribution of a mixture of 15 nominally different polyesters or other polymers as listed above. It may be the result of transesterification when the oxy compound is an alkoxide, such that inorganic atoms become incorporated into the polyester chains. Two or more of such transesterifications may take place. This can lead to an increase in  $M_w$  in a single component or multi-component composition which gives an apparent improvement in thermal stability. 20

Thus according to a further aspect of the present invention there is provided a polymer composition comprising a polymer and optionally at least one second polymer component, and at least one oxygen containing compound of a 25 metal or metalloid selected from Groups IA, IIA, IIIA, IVA, VA, VIA, VIIA, VIII, IB, IIB, IIIB, VB and VIB of the Periodic Table, provided that when the oxygen containing compound is selected from Group IIB and there are first and second polymer components, if the first polymer component is poly(hydroxybutyrate) the second polymer component is not polycaprolactone. Preferred components and amounts for single component compositions are the same as for the 30 polymer component of two or more component compositions. If there is a single polymer component it is preferably present in the composition in amounts of 5 to 99% w/w.

35 One aspect of the invention is that the average weight average molecular weight ( $M_w$ ) of the transesterified polymer composition may be greater than one of the composition containing no inorganic oxy compounds. It may be in certain circumstances that the mechanical properties of the composition of

the present invention may be raised to a level sufficient for practical use, whereas without the catalyst the composition was not usable.

The composition is preferably one having a higher speed of crystallisation than the untreated polyester.

5 In a second preferred composition the polyester components are not compatible and do not give a single T<sub>g</sub> but the transesterified blend shows a T<sub>g</sub> distinct from and additional to or replacing that of the starting components. The transesterified product thus acts as compatibiliser for the starting components.

10 The invention provides a method of making the composition by mixing the components. The oxy compound may be mixed with PHA granules and melted with them; or mixed into a PHA melt; or mixed with PHA and an organic liquid if solvent processing is used.

15 Preferably the composition is heat treated in the melt to permit one or more of the reactions mentioned above. As an alternative, the composition may be shaped before such reactions or while they are incomplete, and a heat treatment applied to shaped articles. A particular example is the procedure of blending in an extruder followed by granulating and melt-shaping the extrudate.

20 The composition may contain any of the usual polymer processing additives, for example particulate fillers, reinforcing fibres, pigments, nucleating agents and plasticisers.

25 In particular one or more plasticisers may be present. The ratio of plasticiser to polymer depends on the intended use of the composition. The range 2-40 phr w/w includes most of the likely uses. For making effectively rigid but not brittle articles the range 5-20 especially 6-12, phr w/w is generally suitable.

Any of the known plasticisers for these polymers are suitable and any plasticisers which are found to plastise these polymers subsequent to this invention would be suitable for use herein. Examples of suitable plasticisers are:

- 30 (a) high boiling esters of polybasic acids, such as phthalates, isophthalates, citrates, fumarates, glutamate, phosphates or phosphites. The esterified radicals may be for example C<sub>1</sub>-C<sub>12</sub> alkyl, aryl or aralkyl. Particular examples are dioctyl-, dibetyl- and dirindcyl- phthalates and dialkylalkylene oxide glutamate (Plasthall 7050);
- 35 (b) high boiling esters and part- of polyhydric alcohols, especially glycols, polyglycols and glycerol. The acid derived radicals of the ester typically contains 2-10 carbon atoms. Examples are triacetin, diacetin and glyceryl dibenzoate;



(c) aromatic sulphonamides such as paratoluene sulphonamide.

A particularly preferred plasticiser is a doubly esterified hydroxycarboxylic acid having at least 3 ester groups in its molecule. "Doubly esterified" means that at least some of the hydroxy groups of the hydroxycarboxylic acid are esterified with a carboxylic acid and at least some of the carboxy groups thereof are esterified with an alcohol or phenol. Preferably at least the hydroxycarboxylic acid from which the ester is derived is aliphatic or cycloaliphatic. Its backbone structure (that is, apart from carboxy groups) preferably contains 2-6 carbon atoms. It contains preferably 2-4 carboxy groups and 1-3 hydroxy groups; and preferably the number of carboxy groups exceeds the number of hydroxy groups. An example of such a plasticiser is Estaflex\* (acetyltri-n-butyl citrate. (\* Trade mark of ZENECA Limited)

The polymer composition may contain any other of the additives commonly used in polymer processing, for example, pigment, particulate or fibrous or platy filler or reinforcer, and nucleating agents, especially boron nitride, talc, ammonium chloride or DZB/Zn Stearate.

The nucleant is preferably present in amounts in the range from 0.2 to 2 phr.

In a yet further aspect the invention provides a process of making shaped articles by confining, eg in a mould or on a surface or through a die, a composition as defined above, then preferably subjecting it to a temperature at which crystallisation is rapid. The process is operable at significantly shorter cycle times than when using previously available PHA compositions.

The polymer can be used in any of the usual methods for forming articles such as injection moulding, compression moulding, extrusion of fibre or films, extrusion of profile, gas-current spinning, tack spinning, coating melt onto substrate, coating latex onto substrate, shaping solution in volatile solvent.

Examples of shaped articles made by such methods include films especially for packaging, coated products (such as paper, paperboard, non-woven fabrics), fibres, non-woven fabrics, extruded nets, personal hygiene products, bottles and drinking vessels, agricultural and horticultural films and vessels, slow-release devices, ostomy bags. Alternatively, the polymer composition with suitable additives can be used as an adhesive.

Thus, the present invention provides method of increasing compatibility of different polyesters in polymer blends and hence a method of improving the physical properties of such blends. The inorganic oxygen containing compounds which bring about these improvements, which may be acting as

transesterification catalysts, can also be used to maintain or increase the molecular weight of a blend of the same or different polymers or to increase the resulting melt viscosity of blends of polymers whose individual components have widely differing melt viscosities. These advantageous properties are described in the following examples which are illustrative of the present invention and do not limit the scope of the invention.

## EXPERIMENTAL METHODS

### Melt Processing

The polymeric components plus oxy compound were powder blended and melt processed in a Betol single screw extruder. For blends of HB homopolymer with HB/HV copolymers (Examples 1 and 2) the barrel zone temperatures were set at 140, 160 and 180°C respectively. The materials were extruded through a 5mm diameter circular die and granulated to polymer chip. The chips were injection moulded into tensile or impact test bars. The tensile bars were of gauge length 40mm with typical cross-sectional areas of 2.4 x 5.3mm. The impact bar dimensions were 4.45 x 13.0 x 118mm.

### Mechanical Tests

Tensile testing was on an Instron 1122 fitted with a Nene data analysis programme. A cross-head speed of 10mm min<sup>-1</sup> was used. Izod impact strength was determined using a Zwick pendulum apparatus. The impact bars were notched at 1mm radius.

### Thermal Analysis

Differential Scanning Calorimetry (DSC) was used. A Perkin Elmer DSC-7 was operated under programmed heating control from 20 to 200°C at 20°C min<sup>-1</sup> to measure melting behaviour. Crystallisation behaviour was monitored by cooling from 200 to 20°C at 20°C min<sup>-1</sup>. From these measurements the melting peak temperature ( $T_{m \text{ peak}}$ ) and the crystallisation peak temperature ( $T_{cryst}$ ) and enthalpies of fusion and crystallisation  $\Delta H_{fus}$  and  $\Delta H_{cryst}$  were determined. Glass transition temperatures  $T_g$  were measured by heating from 20 to 200°C at 100°C min<sup>-1</sup>. The molten material was rapidly quenched to -45°C by cooling at 100°C min<sup>-1</sup>. The amorphous sample was then reheated to 100°C at 20°C min<sup>-1</sup>. The glass transition was the point of inflexion in the heating trace.

This invention is illustrated by the following Examples, in which these abbreviations will be used:

HB homopolymer = poly-3-R-hydroxybutyric acid of  $M_w$  558000,  
made by fermentation using A.eutrophus.  
(Formula I,  $m = 3$ ; CH<sub>3</sub> side chains)

- HB HV copolymer = copolymer of poly-3-R-hydroxybutyric acid (HB) and 3-R-hydroxyvaleric acid, made by fermentation using A.eutrophus with substrate containing propionic acid. (Formula I, m = partly 3, partly 4; CH<sub>3</sub> and C<sub>2</sub>H<sub>5</sub> side chains).
- 5 73B/27V copolymer consisting of 73 mol% 3-R-hydroxybutyrate units and 27 mol % 3-R-hydroxyvalerate units.
- 80B/20V analogous.
- 10 PLA polylactic acid of M<sub>w</sub> = 686000.
- phr weight of additive "per hundred parts by weight of resin" (ie polymer)

**EXAMPLE 1**

HB homopolymer blended with 73B/27V copolymer.

- 15 Each blend contained equal weights of the polymers and 1 phr of additive:

- A tetra-n-propyl titanate (i.e. titanium (IV) tetra-n-propoxide);
- B tetra-n-butyl titanate (i.e. titanium (IV) tetra-n-butoxide); or
- C Sb<sub>2</sub>O<sub>3</sub> (antimony oxide)

- 20 DSC results are shown in Table 1. Additives B and C decreased peak melting temperature by 9°C. On cooling, whereas the copolymer with no additive crystallised very slowly, such that an exotherm was not observed, the composition involving A yielded a pronounced exotherm. Similar but smaller exotherms were observed for the B and C systems. This could be attributed to nucleation and/or chemical modification: see Example 2. Table 1 shows also
- 25 that the additives yielded mechanical properties similar to the control with the added benefit of faster crystallisation.

Table 1

Additive	T <sub>m</sub> peak °C	H fus Jg <sup>-1</sup>	T Cryst °C	H cryst Jg <sup>-1</sup>	M <sub>w</sub> '000	Tens Str MPa	Young's Modulus MPa	Elong at break %	Izod Impact Str/ Jm <sup>-1</sup>
None	176.2	51.8	n.o	0	467	21	506	15.3	95
A	175.8	34.7	71.6	-32.0	489	21	460	15	90
B	167.2	43.1	60.9	-19.0	493	20	477	15	82
C	167.5	45.4	67.1	-8.8	437	21	510	15	87

# EXAMPLE 2

Separate tests of PHB Homopolymer and 73B/27V Copolymer

Samples of each material were mixed with 1phr of additive A, B or C, extruded and granulated as described above. The granules were tested in DSC for melting behaviour; the melt was held at 200°C for 10 min to permit any likely chemical reaction; the melt was then cooled by DSC to observe crystallisation behaviour. The results are shown in Table 2.

Table 2

% HV	Additive	Melting		Crystallisation	
		T Peak °C	H fus J g <sup>-1</sup>	T cryst °C	H cryst J g <sup>-1</sup>
0	None	172.0	92.5	60.7	- 48.0
0	A	172.4	72.7	64.1	- 53.9
0	B	173.3	83.6	63.4	- 48.1
27	None	114.8	70.4	n.o.	0
27	C	113.6	69.2	n.o.	0
27	A	114.2	79.7	n.o.	0
27	B	114.0	79.9	n.o.	0

Key n. o. = not observed

It is evident that the additives have little effect on the melting or crystallisation of either polymer taken separately. However, taking these results with those of Example 1 it is evident that the presence of homopolymer and additive is necessary to promote crystallisation of the copolymer.

### EXAMPLE 3

PHB Homopolymer blended with 80B/20V Copolymer

The procedure, additives and proportions defined in Example 1 were used.

DSC results and the mechanical properties are summarised in Table 3.

The melting point trends were the same as in Example 1. The 20% HV copolymer crystallised more rapidly and a crystallisation exotherm of -10.83 Jg<sup>-1</sup> was observed for the control. The reaction mixtures containing A and B yielded much higher crystallisation energies suggesting that these reaction conditions had produced a faster crystallising composition. Similar trends to those given in Example 1 were observed in mechanical properties.

Table 3

Additive	T peak	H fus	T cryst	H cryst	M <sub>w</sub> '000	Tens str MPa	Young's Modulus MPa	Elong at break %	Izod Impact Str/ Jm <sup>-1</sup>
None	175	69.5	62.41	-10.83	458	27	730	12.0	79
A	173	70.06	60.8	-21.60	473	26	670	12.0	74
B	167	49.19	68.23	-28.37	462	26	665	12.0	73
C	167	53.1	65.11	-11.52	447	26	771	10.0	54

## EXAMPLE 4

## 73B/27V Copolymer with Poly-L-lactic Acid (PLA)

Each blended composition contained equal weights of the polymers and 1phr of additive B or C.

- (a) The materials were melt processed in a Betol extruder with barrel zone temperatures set at 158, 189 and 208 respectively. The polymer was extruded through a 5mm diameter circular die heated to 208°C. The extrudate was cut to form moulding feed granules.
- (b) The granules were, to promote further reaction, melted and then heated at 200°C for 10 min. The material was then rapidly cooled and its Tg(s) measured as described.

Results are shown in Table 4.



Table 4

Additive	Extrudate			After Further Heating		
	T <sub>g</sub> (1) PHB/PHV	T <sub>g</sub> (2)	T <sub>g</sub> (3) PLA	T <sub>g</sub> (1) PHB/PHV	T <sub>g</sub> (2)	T <sub>g</sub> (3) PLA
None	-5.3	-	59.9	-7.01	-	55.5
B	-5.0	-	60.1	-6.4	-	57.13
C	-5.9	-	58.5	-7.8	24	54.1

The PHBV and PLA are mutually incompatible in the melt and amorphous phases as is evident from the multiple T<sub>g</sub> corresponding to those of the PHBV and PLA components respectively. For materials compatible in the amorphous and melt phases a composition-dependent T<sub>g</sub> may be calculated using the Fox equation (T<sub>g</sub> Fox - Bull. Am. Phys. Soc. 123, 2, 1956)

$$\frac{1}{T_g(\text{blend})} = \frac{W(\text{PHBV})}{T_g(\text{PHBV})} + \frac{W(\text{PLA})}{T_g(\text{PLA})}$$

For a 50:50 PHBV/PLA blend, the predicted T<sub>g</sub> for a compatible phase is approximately 24°C (assuming T<sub>g</sub> = -5°C and 60°C for the individual PHBV and PLA components respectively).

This estimate corresponds very well to the intermediate T<sub>g</sub> observed for the antimony oxide system. This suggests that heating promoted a chemical change within a proportion of the composition and produced a compatible polymer system.

#### EXAMPLE 5

PHB homopolymer and PHBV containing 21% HV

Each blended composition contained equal weights of the polymers and 1phr of boron nitride. The materials were melt processed in a Betol extruder with barrel zone temperatures set at 150, 160 and 170°C respectively using methods as previously described. Tensile test bars were prepared as hereinbefore described. The samples were tested after a 1 month post-moulding.

Table 5 1 MONTH TEST DATA

Blend	I	II	III	IV	V	VI
A	295000	88300	3.35	78.25	715.7	13.12
B	385000	110000	3.50	103.75	648.7	17.80
C	362000	100000	3.59	121.25	609.3	18.56

**Key**

- I  $M_w$  (weight average molecular weight)  
II  $M_n$  (number average molecular weight)  
III  $M_w/M_n$   
IV 1mm notched IZOD Impact Test ( $Jm^{-1}$ )  
V Young's Modulus (MPa)  
VI Elongation to break (%)

**EXAMPLE 6**

The experiment detailed in Example 5 was repeated with a blend of PHBV copolymer (6%HV) and polycaprolactone (PCL) (Tone 787 Union Carbide Limited) and a range of catalysts. Each blend contained 80% PHBV and 20% PCL, 1phr boron nitride and 1 phr of catalyst. The control samples contained all the ingredients except the catalyst. Tensile bars were made from the blend. The combinations of polymer blend and catalyst are given in Table 6 with the results of elongation to break tests given as the percentage increase in elongation to break compared to the control sample. The samples were 6 weeks old when the test was carried out.

Table 6

Blend	Catalyst	E to B %
1	calcium acetate	6.6
2	calcium carbonate	40
3	aluminium oxide acidic	40
4	aluminium oxide basic	36
5	aluminium oxide active	25
6	aluminium isopropoxide	20
7	titanium IV propoxide	83
8	titanium IV butoxide	40
9	titanium IV propoxide and methyl propanoate (30%)	10
10	titanium IV butoxide and ethylene glycol (24%)	100
12	titanium IV butoxide and methyl propanoate (50%)	36
13	none	0

**EXAMPLE 7**

The results described in the previous examples provide evidence that titanium propoxide and titanium butoxide may be transesterifying the polymer blend. An experiment was set up to assess the effects of such catalysts on the melt viscosity of the molten blend.

Extruded granule samples containing 5g of the polymer blends shown in Table 7 were rapidly charged into a standard melt flow grader (manufactured by Davenport UK). This was fitted with a standard die of length 8 mm and diameter 2.095 mm and preheated to  $180 \pm 0.5^\circ\text{C}$ . After 4.5 minutes heating up time, a 2.2 kg weight was applied to the piston. The resulting extrudate was cut off after the 5 minute time interval and discarded. Cut-offs were then subsequently taken at 1 minute intervals and weighed. In polyolefins, the melt flow index (MFI) is defined as the weight of polymer extruded under standard

conditions over a 10 minute period.

In this experiment, the "instantaneous" melt flow index is defined as 10 times the weight of polymer extruding from the die in a 1 minute time period. This is because, under the conditions used, poly(hydroxybutyrate-co-hydroxyvalerate) polymers degrade and the MFI increases with time. The doubling time  $T_d$  is defined as the time interval over which the MFI value is seen to increase by a factor of two.

When the logarithms of the "instantaneous" MFI's were plotted, a straight line relationship was observed. This allowed the MFI at 5 minutes heating time and the  $T_d$  to be calculated. The results observed are tabulated below.

Table 7

Formulation				MFI at 5 mins/g	$T_d$ / mins
Catalyst	Catalyst (phr)	Homo- polymer	21% HV copolymer		
None	0	50	50	11.80	1.4
Titanium IV propoxide	1	50	50	5.45	2.47
Titanium IV butoxide	1	50	50	4.03	2.82

The results indicate that the 5 minutes MFI is reduced by a factor of two for the formulations containing titanium catalysts. The time taken for the MFI to double also increased significantly.

As high MFI's are associated with low melt viscosities, the use of the catalyst system leads to an increase in melt viscosity. This may be explained in two ways. The homopolymer component of the blend has a peak melting point of 175°C and the 21% copolymer has a peak melting point of 144°C. Under the conditions used for the test, the copolymer is in excess of 35°C above its melting point and would be expected to have a very low melt viscosity compared to the homopolymer. Consequently this would tend to plasticise the blend and lead to high MFI's as observed for the system with no catalyst.

The use of catalyst potentially transesterifies the two polymeric components leading to blocks of homopolymer along the copolymer chain and

vice-versa. This would be expected to lead to a higher melt viscosity and consequently lower MFI's. This is what is observed in the results of this example.

In addition to this in the formulations containing catalyst the rate of increase of MFI with time at temperature becomes less pronounced. This could be interpreted in terms of a thermal stability effect with the transesterification process leading to a preservation of molecular weight and competing with the normal scission processes observed during the thermal degradation of poly(hydroxybutyrate-co-hydroxyvalerate).

To test this theory, thermal degradation studies were conducted using a differential scanning calorimeter (Perkin Elmer DSC4) as the heat source. The degradations were done under nitrogen. Samples of 10mg size were taken for the formulations listed in Table 8 and encapsulated in aluminium pans. The samples were rapidly heated to 180°C at 100°C min<sup>-1</sup> and maintained at temperature for a range of set times ranging from 1 to 10 minutes. The material was then rapidly cooled at -200°C min<sup>-1</sup> to room temperature and the molecular weight of the resulting polymer measured.

Tanfield (ref: Physical Chemistry of Macromolecules, (1961) pages 612-619. Pub. John Wiley.) describes methods for measuring the rate constant for random scission degradation.

In the early stages of degradation

$$\frac{1}{x_w} = \frac{1}{(x_w)_0} + \frac{k_2 t}{2}$$

$x_w$  = the weight average degree of polymerisation of the degraded polymer at time t

$(x_w)_0$  = the weight average degree of polymerisation of the polymer at t = 0

and k = the rate constant describing the rate of bond scission.

A plot of the 1/ $x_w$  against t yields a linear plot and allows k to be calculated as 2 x the gradient.

Table 7

Catalyst	Catalyst Level	Homopolymer	21% HV Copolymer	k /s <sup>-1</sup>
None	0	50	50	1.56x10 <sup>-6</sup>
Titanium IV Butoxide	1	50	50	1.05x10 <sup>-6</sup>

5

The results suggest that the rate of bond scission is lower for the system containing catalyst and that consequently it may be acting as a route to thermal stabilisation.



## CLAIMS

- 1 A polymer composition comprising a first polyester component which is at least one polyhydroxyalkanoate, and a second different polymer component, and at least one oxy compound of a metal or metalloid selected from Groups IA, IIA, IIIA, IVA, VA, VIA, VIIA, VIII, IB, IIIB, VB and VIB of the Periodic Table.
- 2 A polymer composition comprising a first polyester component which is at least one polyhydroxyalkanoate, and at least one second polymer component, and at least one oxygen containing compound of a metal or metalloid selected from Group IIB of the Periodic Table; provided that when the first polyester component is poly(hydroxybutyrate) the second polymer component is not polycaprolactone.
- 3 A polymer composition comprising a first polymer component and optionally at least one second polymer component, and at least one oxygen containing compound of a metal or metalloid selected from Groups IA, IIA, IIIA, IVA, VA, VIA, VIIA, VIII, IB, IIB, IIIB, VB and VIB of the Periodic Table, provided that when the oxygen containing compound is selected from Group IIB and there are first and second polymer components, if the first polymer component is poly(hydroxybutyrate) the second polymer component is not polycaprolactone.
- 4 A polymer composition according to any of claims 1 to 3 wherein the second polymer component is selected from (a) a different production batch of same PHA; or (b) a PHA of different composition; or (c) a PHA as in (a) or (b) but with a different history; or (d) a head-to-tail polyester or a substantially stoichiometric head-to-head tail-to-tail polyester; or (e) a synthetic polyester having only alcohol or phenol reactivity or only acyl reactivity; or (f) other polymers having potential acylatable and or esterifiable groups.
- 5 A polymer composition according to any of claims 1 to 4 wherein the second polymer component is selected from polyhydroxyalkanoate polycaprolactone, polylactides, and polyesters containing combinations of dicarboxylic acids or derivatives thereof with diols, cellulose and cellulose acetates or butyrates, polypeptides, proteins, polyamides, or copolymer of succinic acid and butylene glycol.
- 6 A polymer composition according to any of the preceding claims wherein the second polymer component is selected from the group: polyhydroxybutyrate, polyhydroxyvalerate, polyhydroxybutyrate-co-valerate, polycaprolactone, polylactic acid and copolymer of succinic acid and butylene glycol.

- 7 A polymer composition according to any of the preceding claims wherein the first polyester component is selected from polyhydroxybutyrate, polyhydroxyvalerate or polyhydroxybutyrate-co-valerate.
- 8 A polymer composition according to any of the preceding claims wherein the metal or metalloid is selected from an alkali metal, an alkaline earth metal, aluminium, silicon, phosphorus, titanium, germanium, arsenic, zirconium, tin, zinc, cadmium or antimony.
- 9 A polymer composition according to any of the preceding claims wherein the oxygen containing compound is selected from an alkoxide, phenoxide, enolate, carbonate, acetate or carboxylate.
- 10 A polymer composition according to any of the preceding claims wherein the oxygen containing compound is selected from titanium butoxide, titanium propoxide, antimony trioxide, calcium acetate, calcium carbonate, aluminium oxide acidic, aluminium oxide basic, aluminium oxide active, aluminium isopropoxide, titanium propoxide and titanium butoxide.
- 11 A polymer composition according to any of the preceding claims wherein the inorganic oxygen containing compound is used in a solvent.
- 12 A polymer composition according to any of the preceding claims further comprising one or more reaction products of one or more of the first polyester component, second polyester component, other polyester component (if any) and the oxygen containing compound.
- 13 Shaped articles prepared from a polymer composition as defined in any of the preceding claims.
- 14 Method of improving the melt viscosity of a two or more component polymer composition which comprises including in the composition one or more oxygen containing compounds as defined in any of claims 1 to 12.
- 15 Method of improving thermal stability of a one or more component polymer composition which comprises including in the composition one or more oxygen containing compounds as defined in any of claims 3 to 12.
- 16 Method of improving the physical properties of a two or more component polymer composition which comprises including in the composition one or more oxygen containing compounds as defined in any of claims 1 to 12.
- 17 Method of improving compatibility of polymers in a polymer composition containing 2 or more polymer components which comprises including in the composition one or more oxygen containing compounds as defined in any of claims 1 to 12.
- 18 Method of increasing crystallisation rate of a polymer composition

containing 2 or more polymer components which comprises including in the composition one or more oxygen containing compounds as defined in any of claims 1 to 12.

19 A process of making shaped articles by confining a polymer composition as defined above, then subjecting it to a temperature at which crystallisation is rapid.

20 A process for preparing a polymer composition as defined in any of Claims 1 to 12 which comprises mixing the polymer components and an oxygen containing compound.

21 A composition comprising a first polyester component which is at least one polyhydroxyalkanoate and at least one oxy compound of a metal from an A group of the Periodic Table or of a metal or metalloid from a B group of the Periodic Table, said Group B metal or metalloid having a valency of at least 3.

22 A composition comprising a first polyester component which is at least one polyhydroxyalkanoate and at least one second polyester component which is a different polyhydroxyalkanoate and/or a polymerised hydroxycarboxylic acid containing repeating units each having up to 5 successive carbon atoms in the polymer chain, and at least one oxy compound of a metal from an A group of the Periodic Table or of a metal or metalloid from AB group of the Periodic Table, said Group B metal or metalloid having a valency of at least 3.



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/GB93/02280 <b>(22) International Filing Date:</b> 4 November 1993 (04.11.93) <b>(30) Priority data:</b> 9223351.9 6 November 1992 (06.11.92) GB <b>(71) Applicant (for all designated States except US):</b> ZENECA LIMITED [GB/GB]; Imperial Chemical House, 9 Millbank, London SW1P 3JF (GB). <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only) :</b> HAMMOND, Timothy [GB/GB]; 12 Cragside, Sedgefield, Stockton on Tees, Cleveland TS21 2DQ (GB). <b>(74) Agents:</b> MANNION, Sally, Kim et al.; Group Patent Services Department, P.O. Box 6, Shire Park, Welwyn Garden City, Hertfordshire AL7 1HD (GB).		<b>(81) Designated States:</b> AT, AU, BB, BG, BR, BY, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, LV, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>  <b>(88) Date of publication of the international search report:</b> 7 July 1994 (07.07.94)
<b>(54) Title:</b> POLYMER COMPOSITION CONTAINING POLYHYDROXYALKANOATE AND METAL COMPOUND  <b>(57) Abstract</b>  Polymer compositions are provided which comprise a first polyhydroxyalkanoate component and optionally a second polymer component, the composition have enhanced properties by using an inorganic oxygen containing compound in the composition. The inorganic oxygen containing compound may be acting as a transesterification catalyst.		

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## A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 C08L67/04 C08K3/00 C08K5/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 16, no. 425 (C-982) (5468) 7 September 1992 & JP,A,04 146 952 (AGENCY OF IND SCIENCE AND TECHNOLOGY) see abstract ---	1-5
X	PATENT ABSTRACTS OF JAPAN vol. 12, no. 450 (C-547) (3297) 25 November 1988 & JP,A,63 172 762 (MITSUBISHI RAYON KK) see abstract ---	1-5
X	JP,A,3 157 450 (AGENCY OF IND SCIENCE AND TECHNOLOGY) 5 July 1991 see table 1 -----	1-6



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents:

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# INTERNATIONAL SEARCH REPORT

national application No.

PCT/GB93/02280

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. Claims: 1-13, 20, 22 Composition containing 2 polymers and one metal compound
2. Claims: 14-19 Methods for getting special effects
3. Claims: 21, 3 partially Composition containing 1 polymer and one multivalent metal compound

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
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- ☐ The additional search fees were accompanied by the applicant's protest.
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